



Determination of radioisotopes using ICPMS

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Determination of radioisotopes using ICP-MS

The coupling between chemistry and
instrumentation.

Per Roos
DTU NUTECH

Use of ICP-MS in analysing radioisotopes

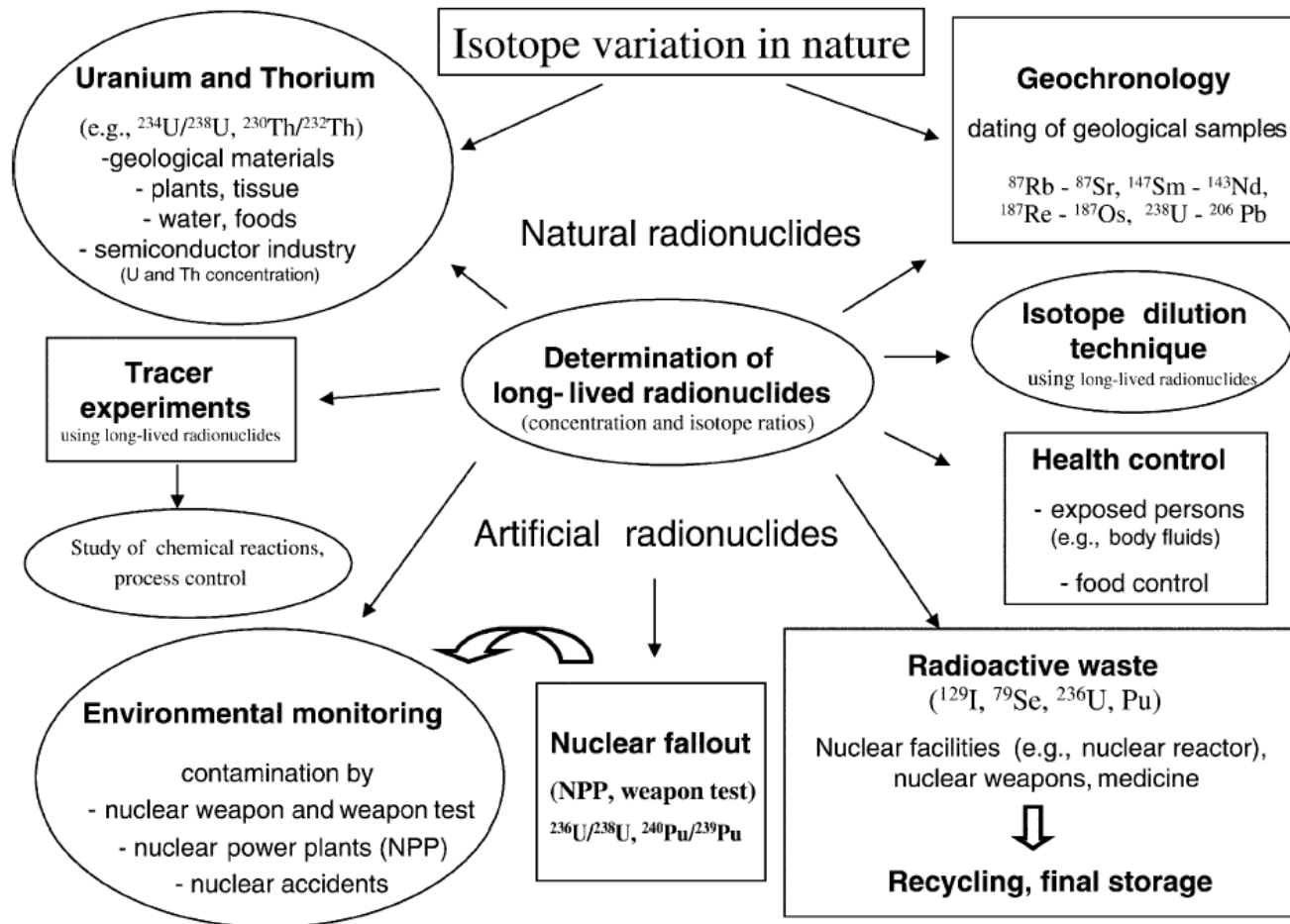
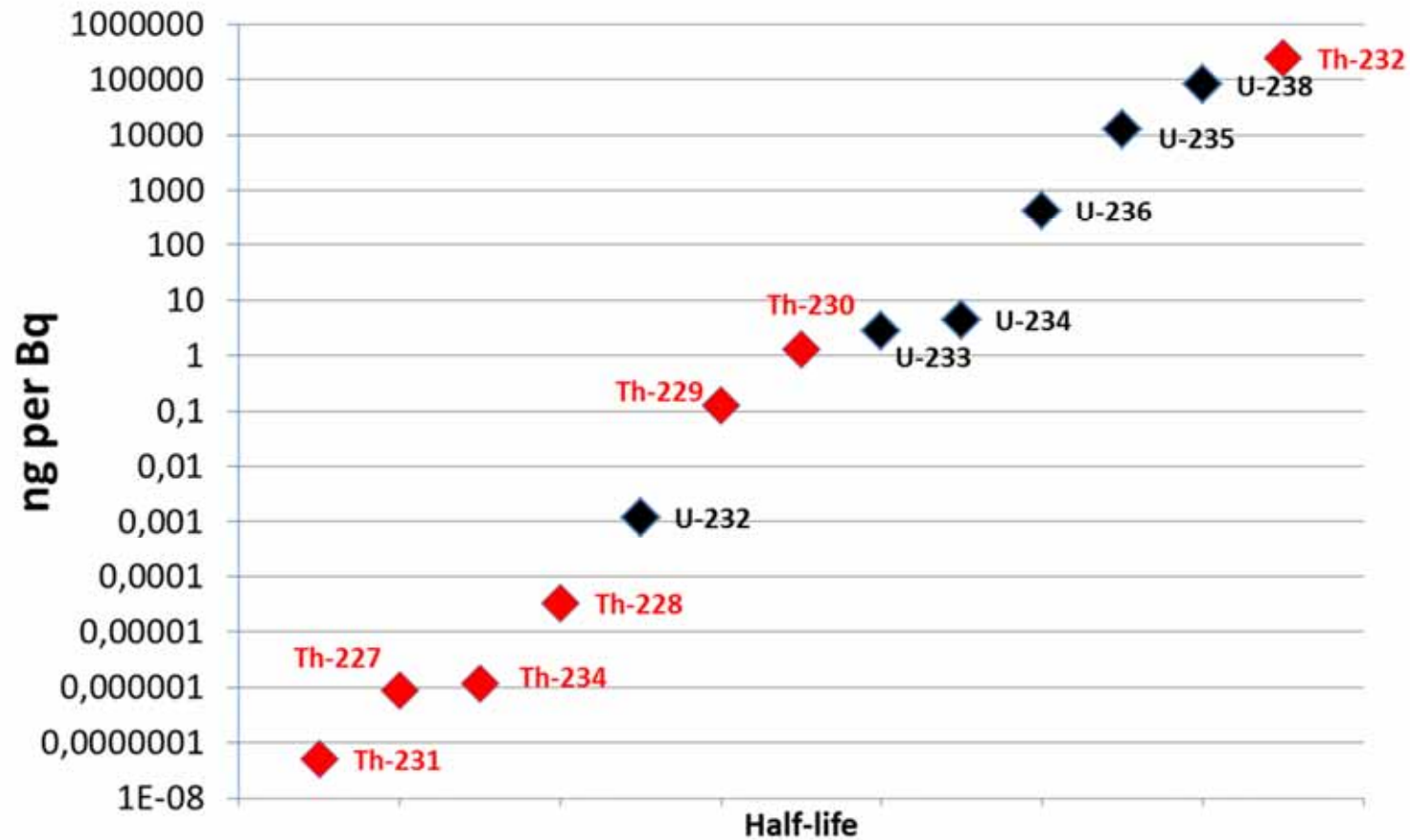


Fig. 1. Overview of application fields for determination of long-lived radionuclides.

Specific activity of U & Th isotopes



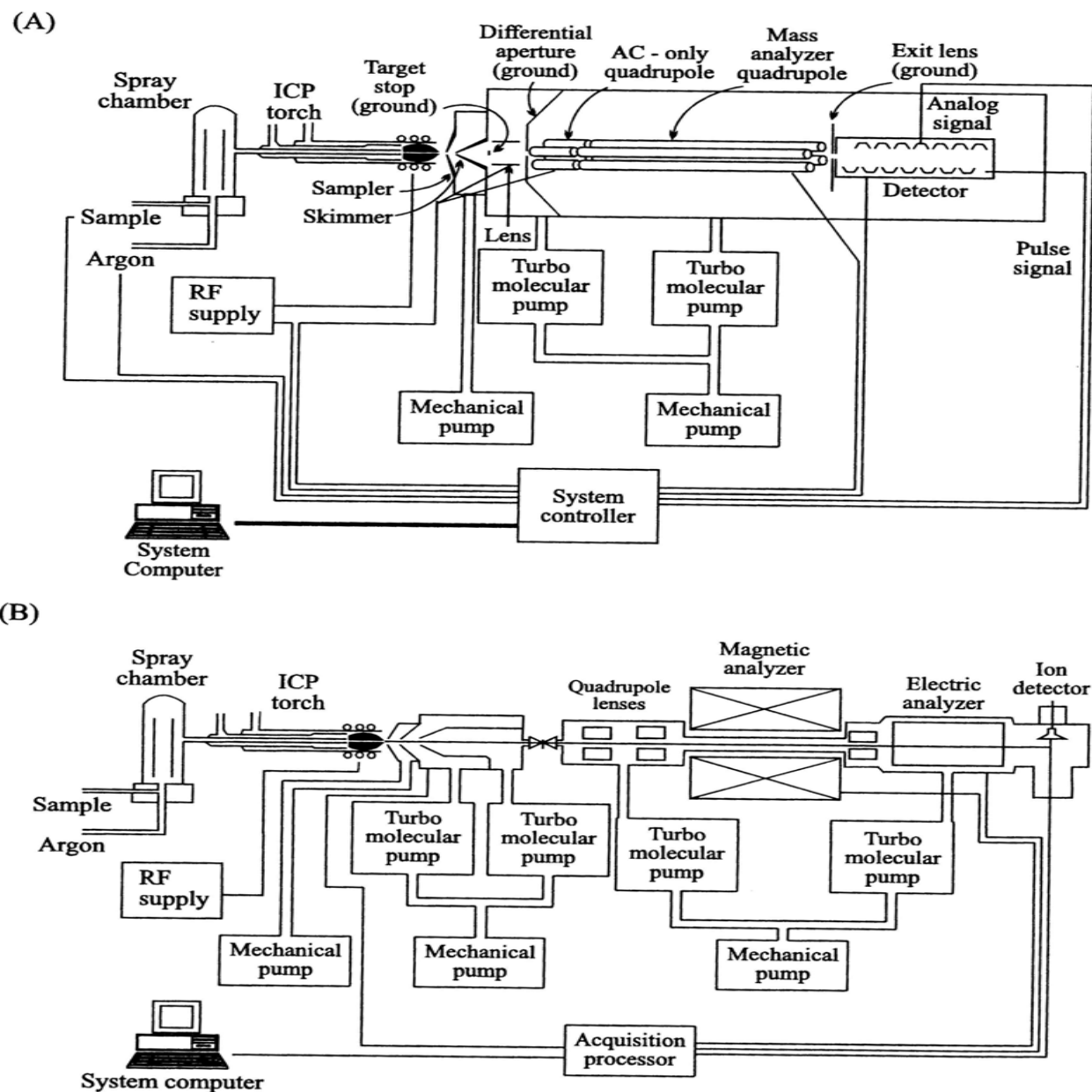


Figure 1.4 (A) Schematic diagram of a quadrupole ICPMS, the Elan 6000. (Courtesy of the Perkin-Elmer/Sciex Corporation.) (B) Schematic diagram of a magnetic sector ICPMS, the JMS-PLASMAX2. (Courtesy of JOEL Incorporated.)

Plasma Trace II – High resolution ICP-MS



Thermo X-series II – Quadrupole ICP-MS



Table 1.3 Distribution of ionization energies among the elements for singly and doubly charged ions. Grouped in steps of 1 eV.

Ionization Energy (eV)	Elements
< 7	Li, Na, Al, K, Ca, Sc, Ti, V, Cr, Ga, Rb, Sr, Y, Zr, Nb, In, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Tl, Ra, Ac, Th, U
7–8	Mg, Mn, Fe, Co, Ni, Cu, Ge, Mo, Tc, Ru, Rh, Ag, Sn, Sb, Ta, W, Re, Pb, Bi
8–9	B, Si, Pd, Cd, Os, Ir, Pt, Po
9–10	Be, Zn, As, Se, Te, Au
10–11	P, S, I, Hg, Rn
11–12	C, Br
12–13	Xe
13–14	H, O, Cl, Kr
14–15	N
15–16	Ar
> 16	He, F, Ne

2⁺ Ions
Ba, Ce, Pr, Nd, Ra
Ca, Sr, La, Sm, Eu, Tb, Dy, Ho, Er
Sc, Y, Gd, Tm, Yb, Th, U, Ac
Ti, Zr, Lu
V, Nb, Hf
Mg, Mn, Ge, Pb
All other elements

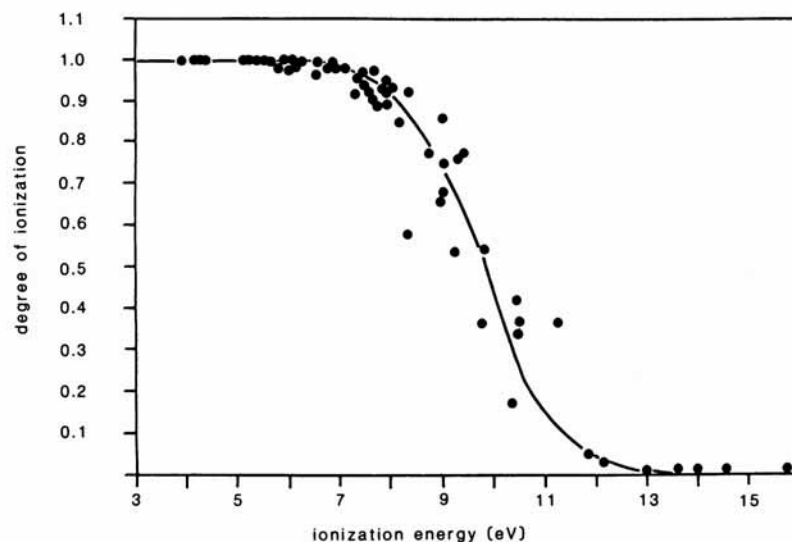
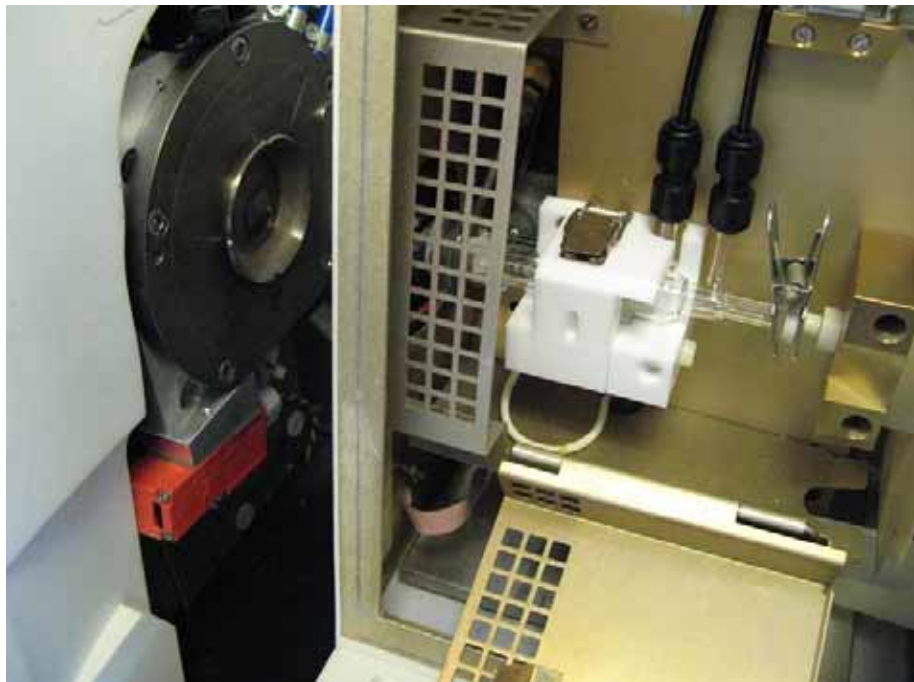


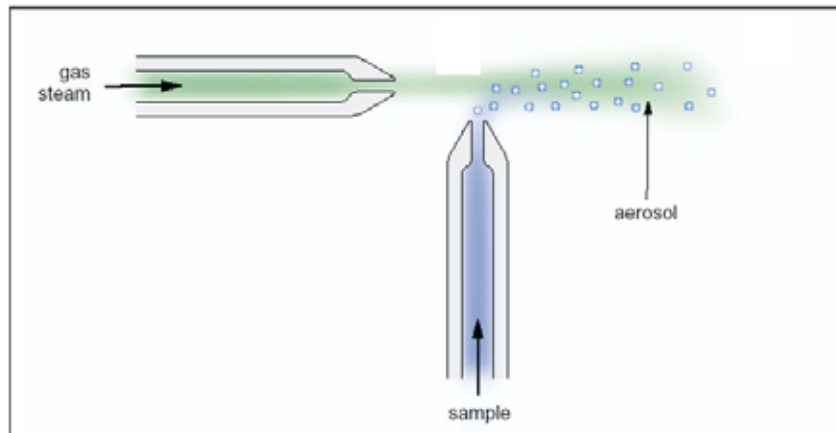
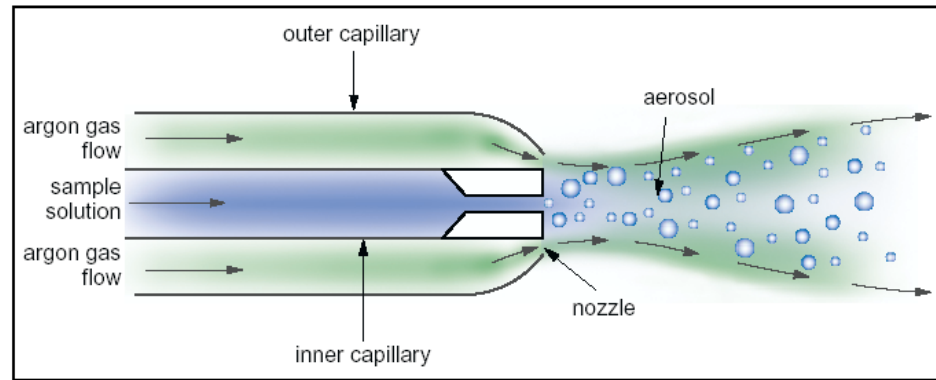
Figure 1.7 Degree of ionization α versus ionization energy for singly charged ions in the ICP. Calculated for a representative selection of 59 elements from the Saha equation, assuming values of T_i of 8000 K and n_e of $2.5 \times 10^{15} \text{ cm}^{-3}$.

Sample introduction



Pneumatic nebulisers

- Concentric nebulisers
- Cross-flow nebulisers



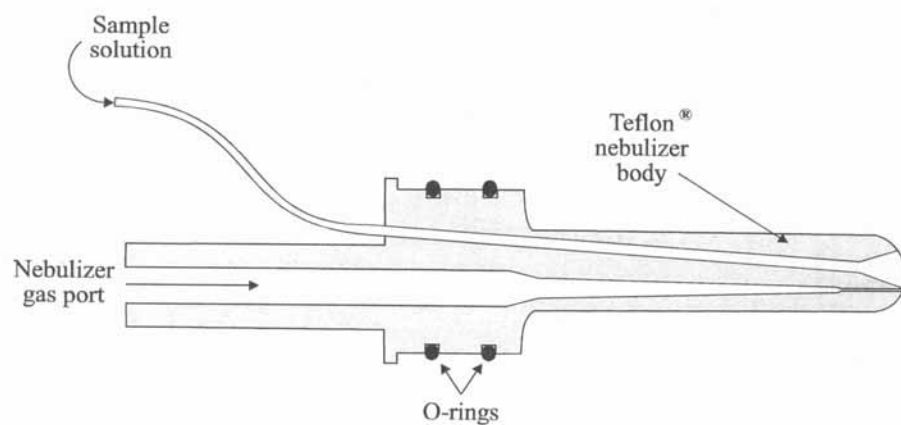


Figure 3.14 Schematic diagram of a Burgener parallel path nebulizer. (Courtesy of Burgener Research Inc.)

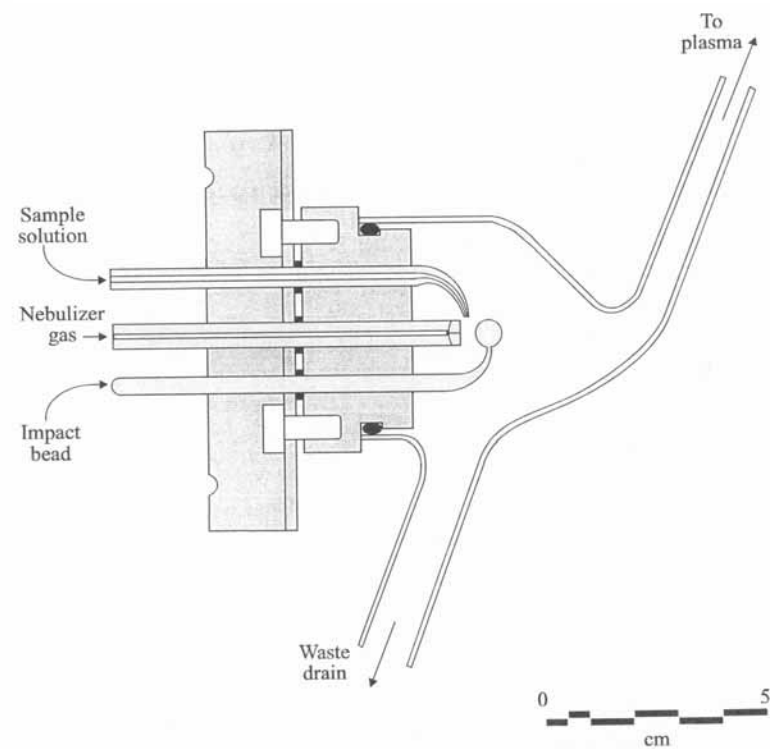


Figure 3.11 The GMK Babington nebulizer, with its glass impactor bead and spray chamber. (Courtesy of Labtam International Pty Ltd.)

The need of a spray chamber

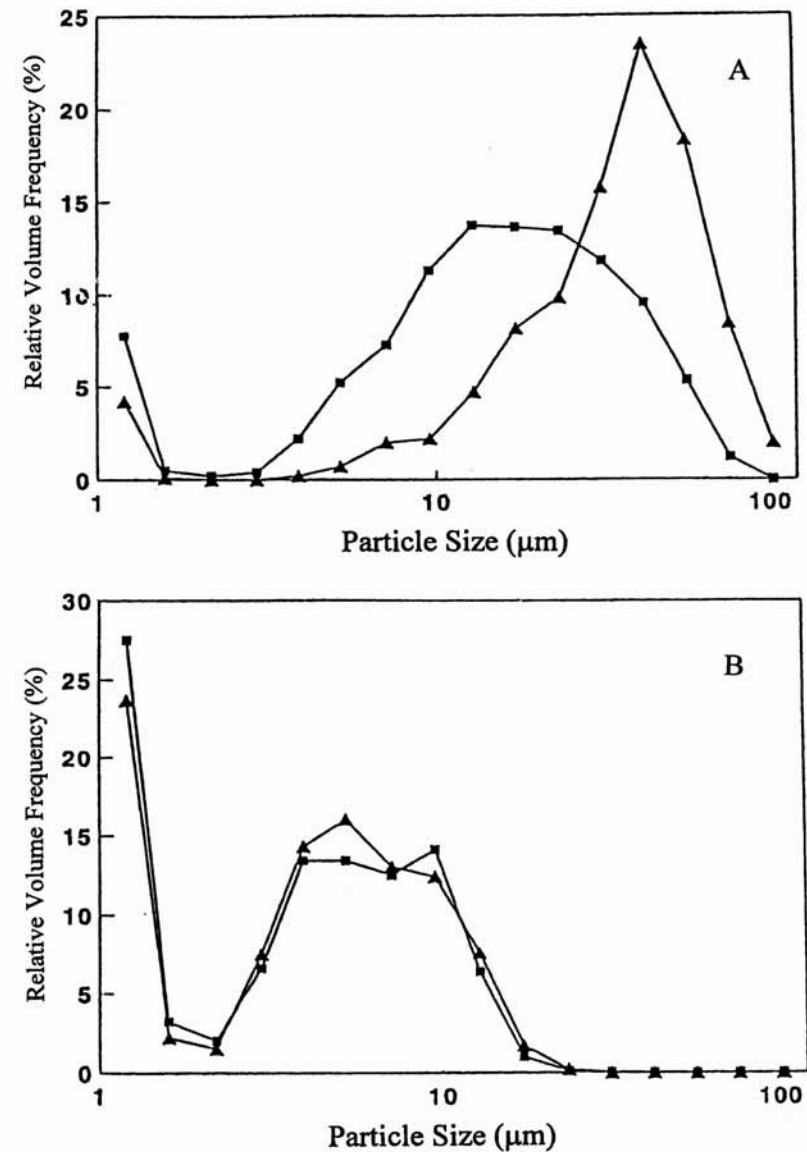
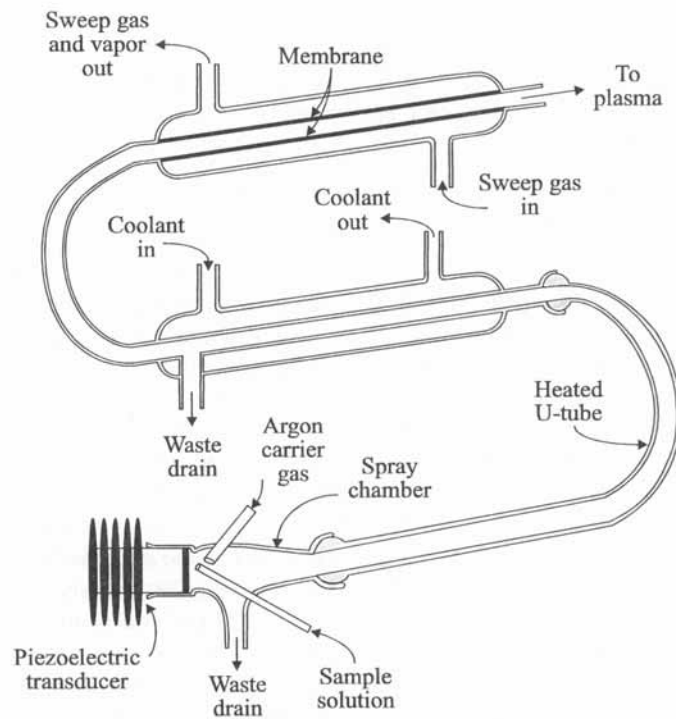


Figure 5.22 Primary and tertiary droplet size distributions for a conventional concentric nebulizer (squares) and a crossflow nebulizer (triangles) obtained with laser Fraunhofer diffraction. (A) Primary aerosol at an injector gas flow rate of 0.7 L/min. (B) Tertiary aerosol at an injector gas flow rate of 1 L/min. For both nebulizers, a double-pass spray chamber was used when the tertiary aerosol was probed. (From Reference 149, with permission.)

High efficiency nebulisers

(B)



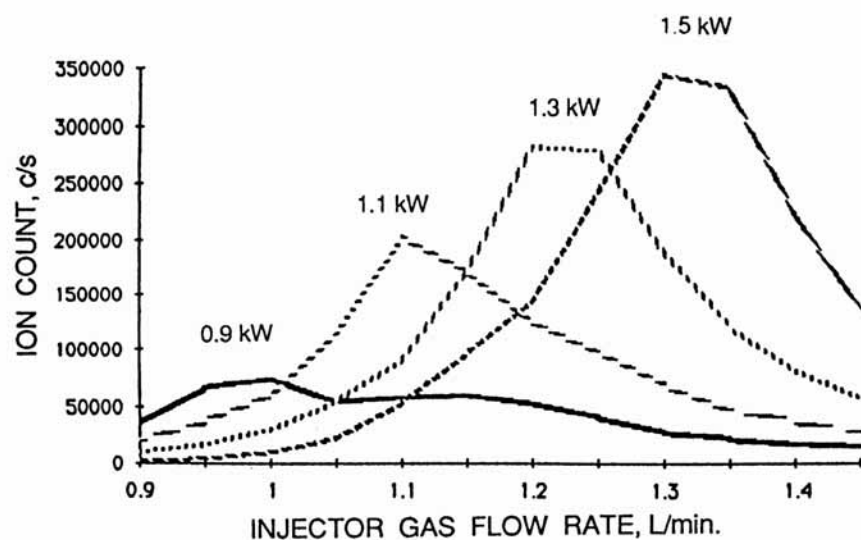


Figure 7.2 Dependence of Ga^+ signal on injector gas flow rate for a range of forward powers. (Sampling depth was 20 mm from the load coil.) (From Reference 60, with permission.)

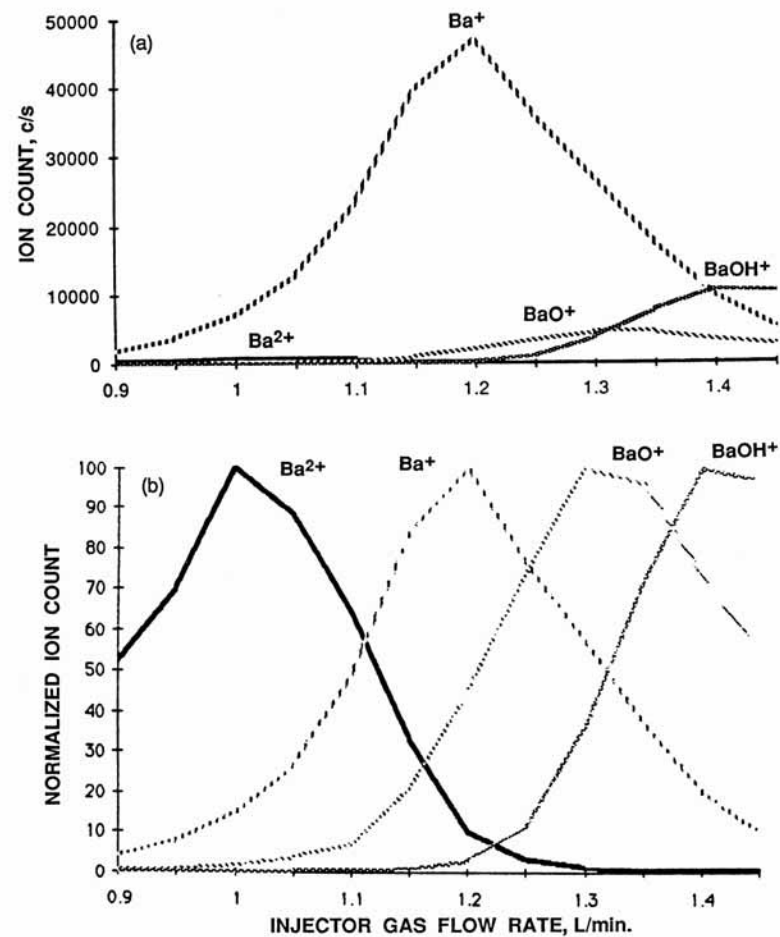
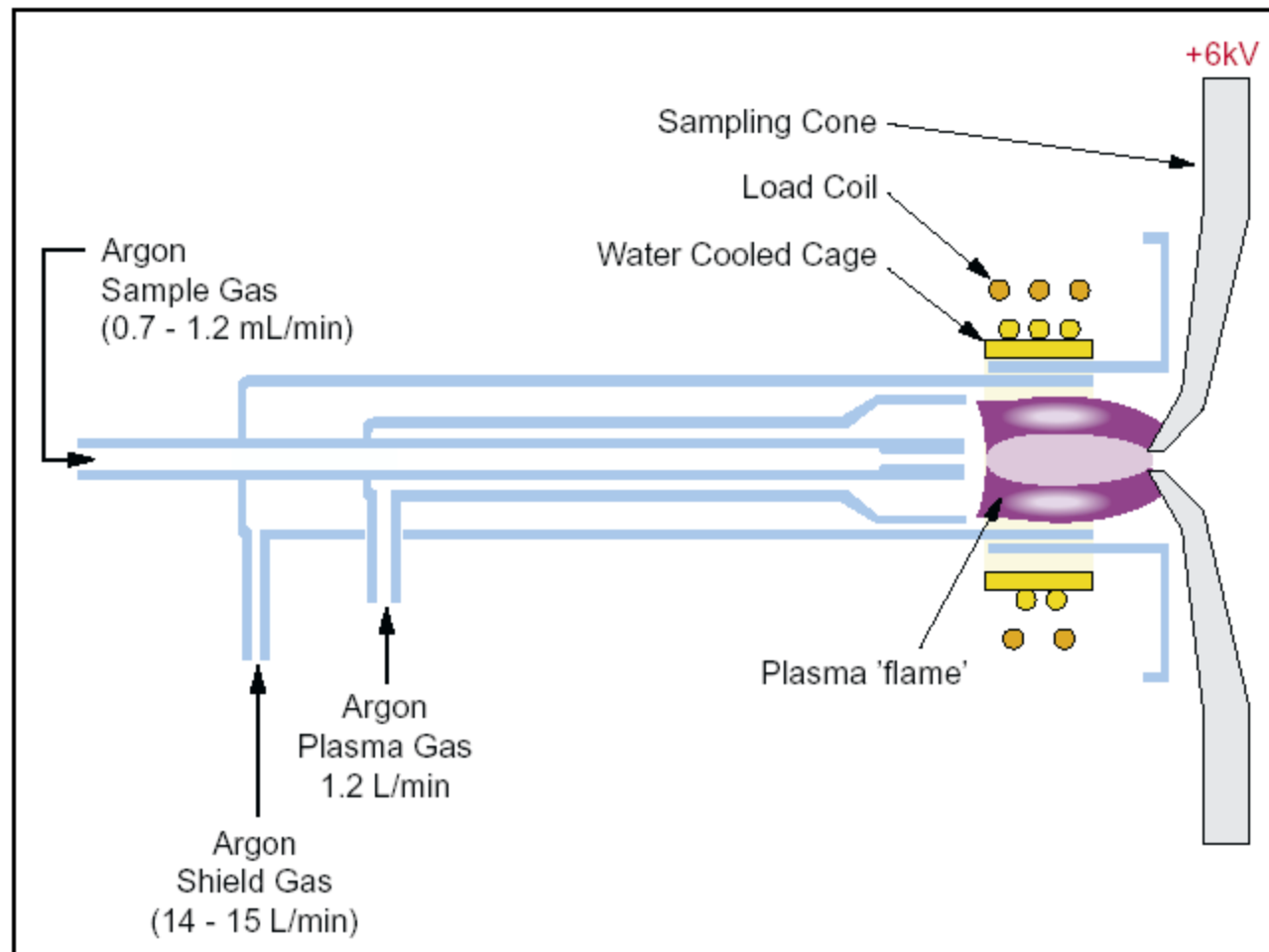
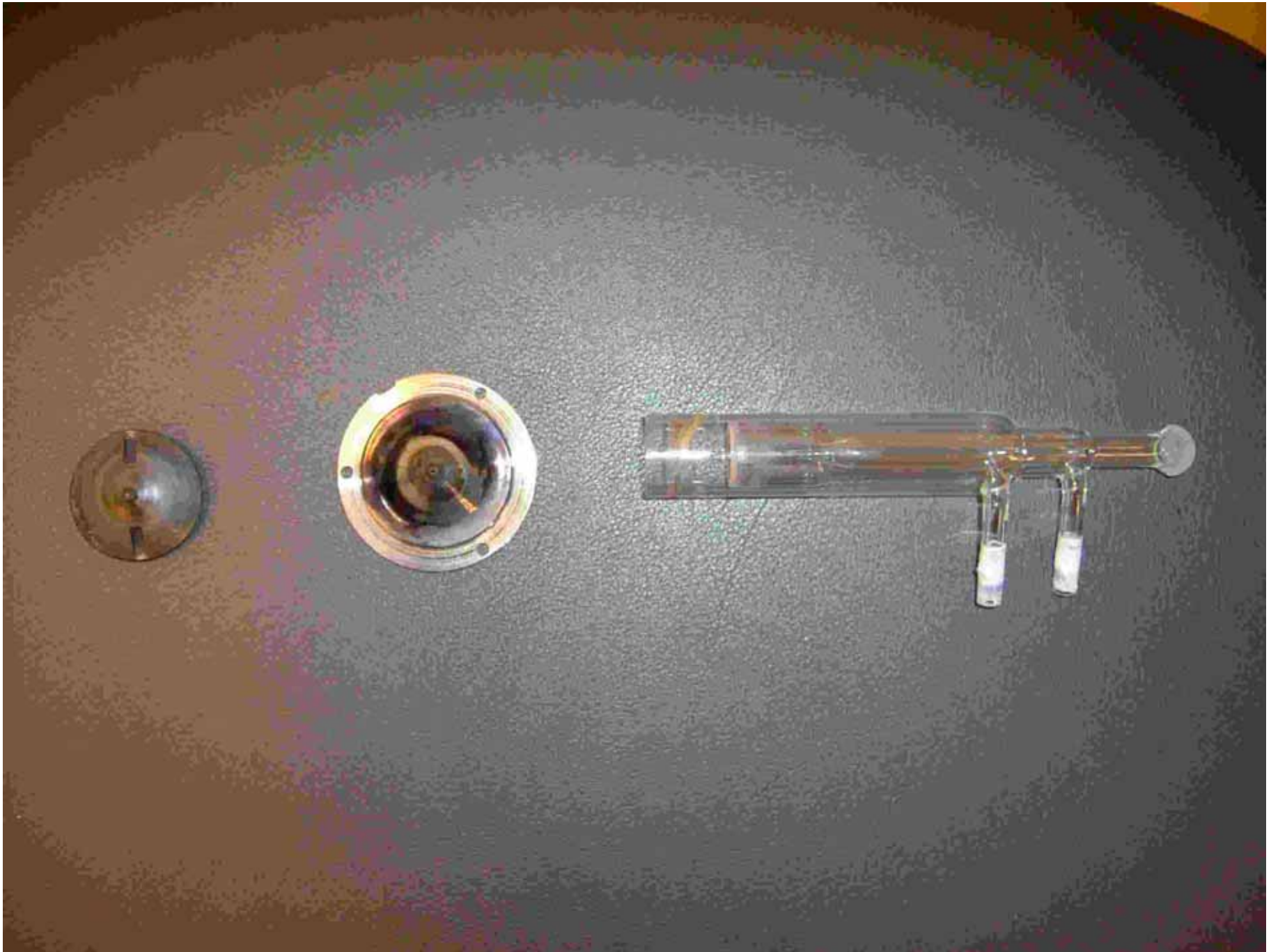


Figure 7.8 Relative (top) and normalized (bottom) plots of signal as a function of injector gas flow rate at a forward power of 1.3 kW for barium species. (From Reference 91, with permission.)





Pressure difference at interface region

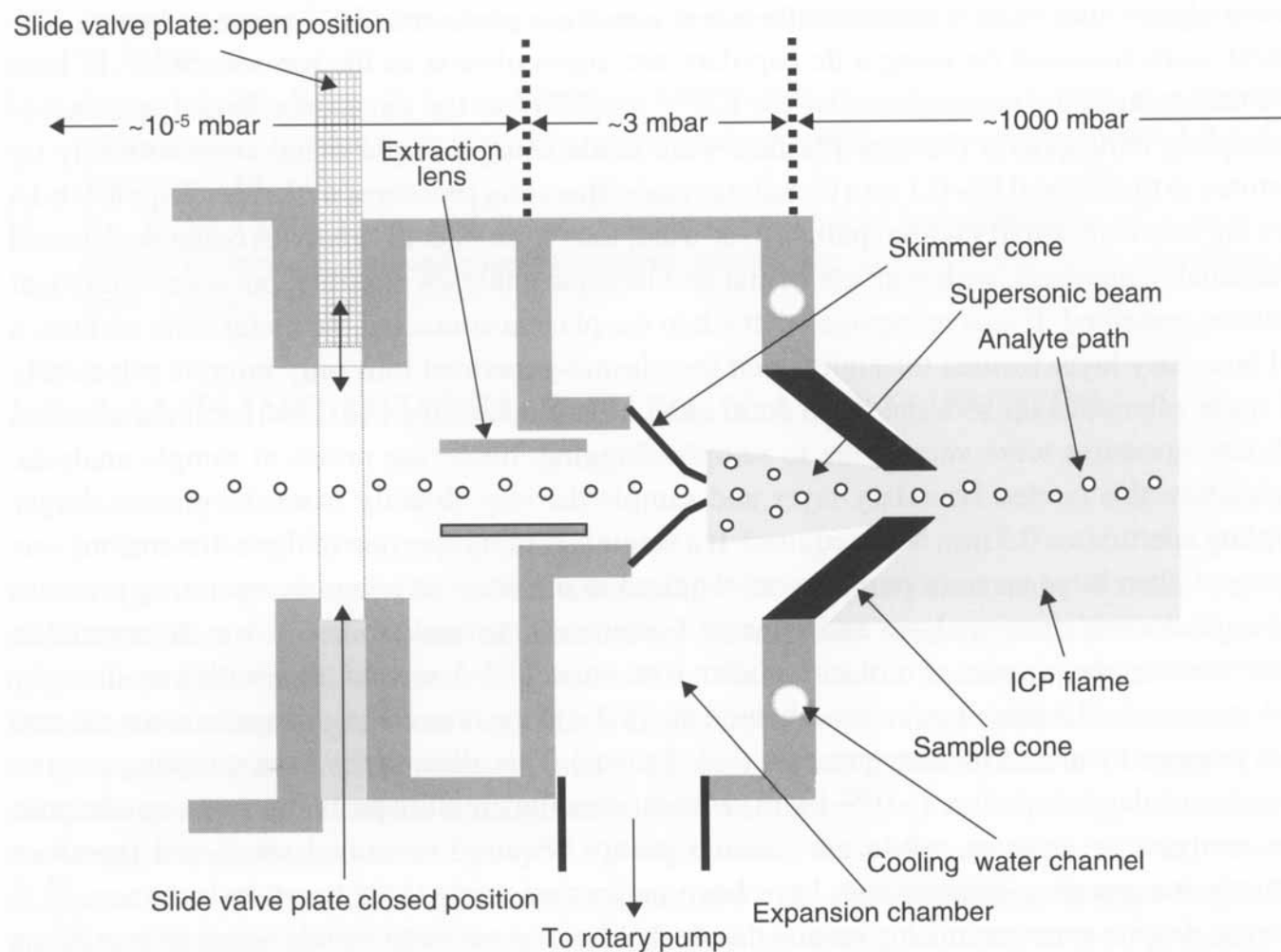
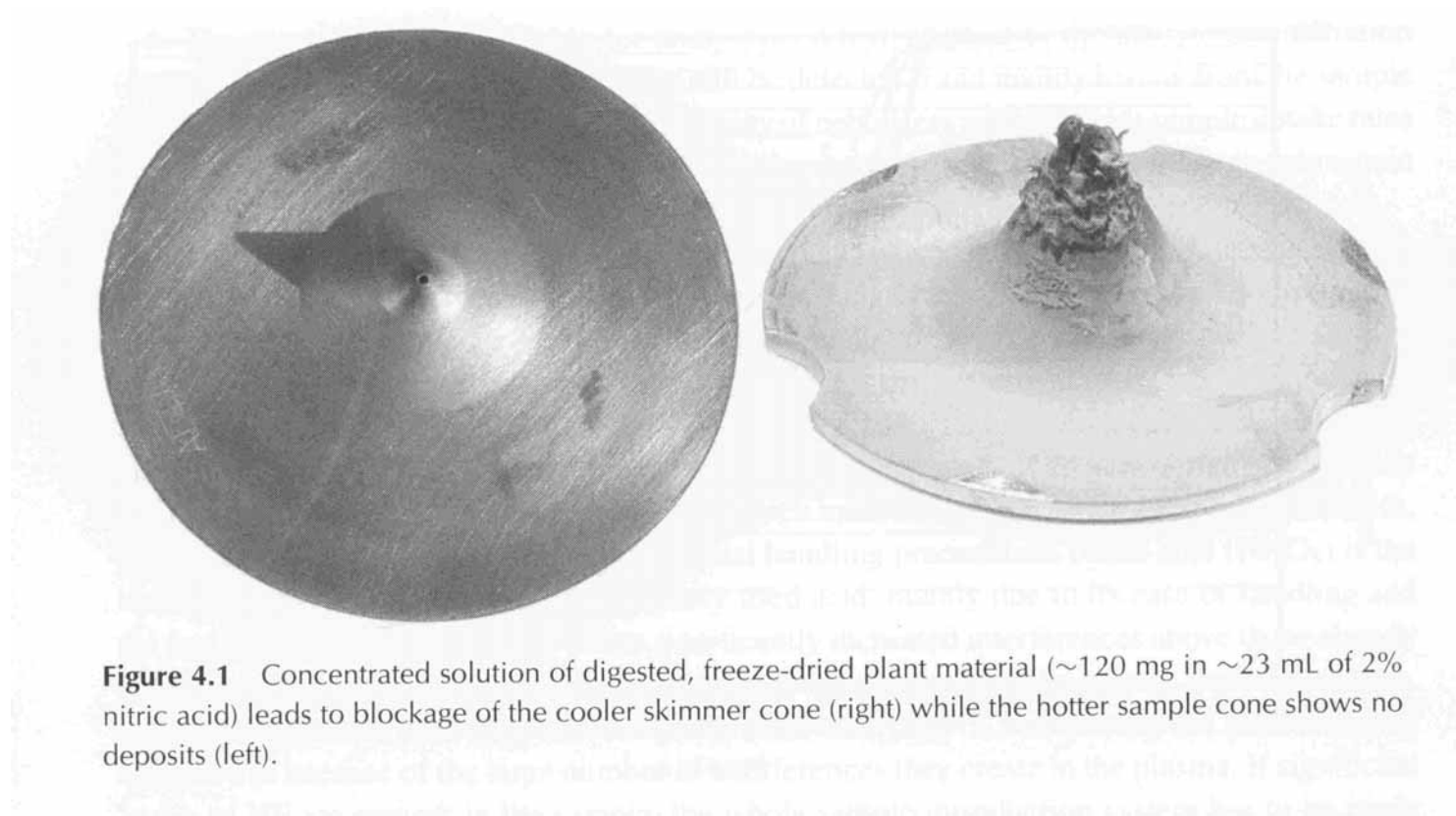


Figure 1.4 A cross section through a typical ICP-MS ion sampling interface region.

Clean samples & need for matrix removal



Mass discrimination at interface

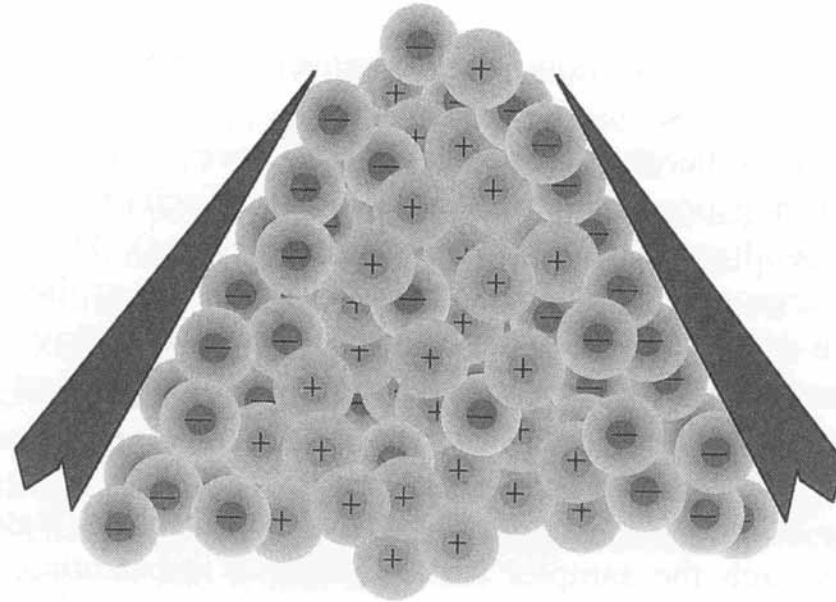


Plate 2 Under high charge density conditions, the Debye spheres of the charged particles overlap and the particles experience modified fields (they are “shielded” from the applied electrostatic field). Because of their higher mobility, electrons preferentially diffuse to the walls where an electron sheath forms. Due to the electron diffusion, a net positive charge density remains on axis and the resultant space charge field is positive. See color plate.

Detectors

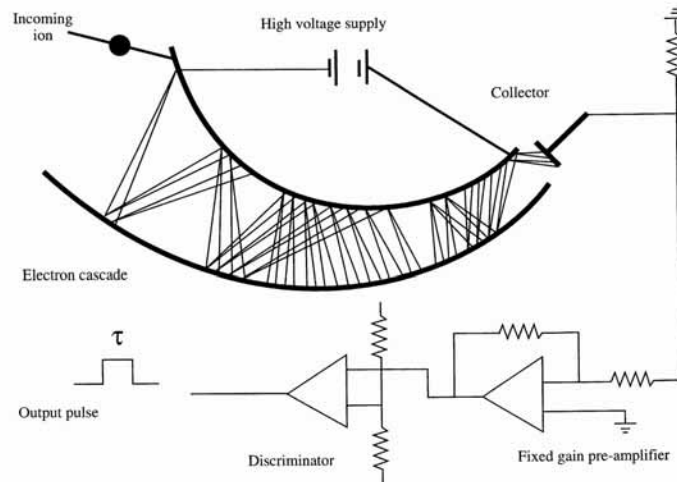


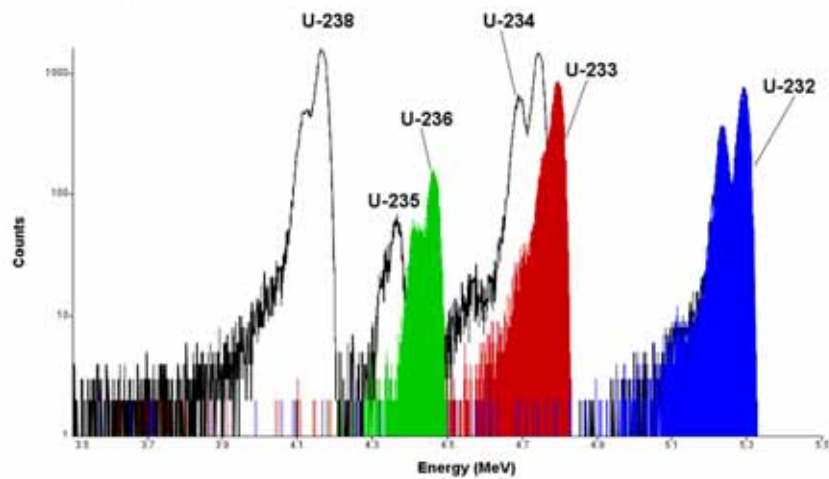
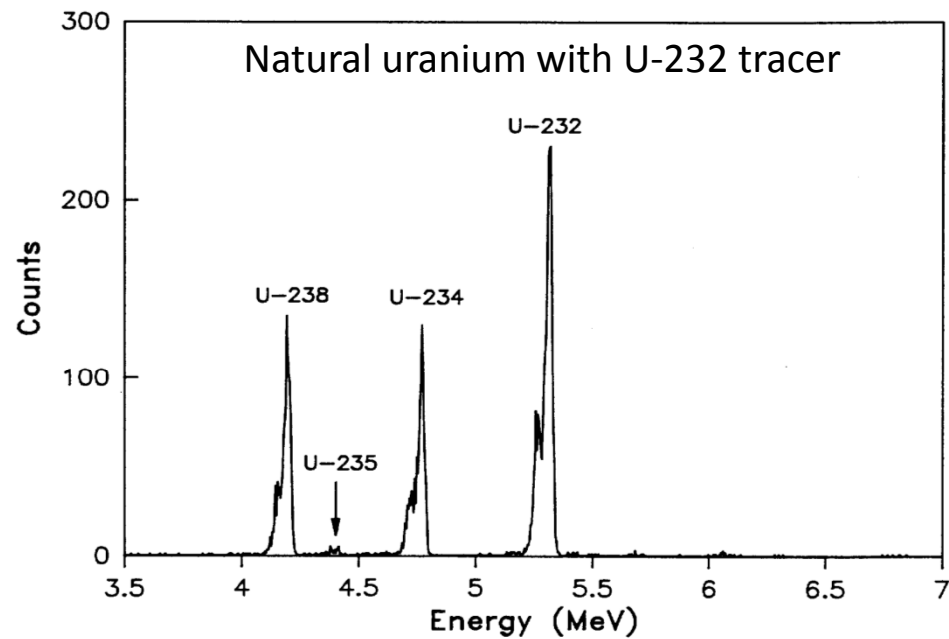
Figure 6.29 Continuous dynode electron multiplier.



Radioisotopes – focus on:

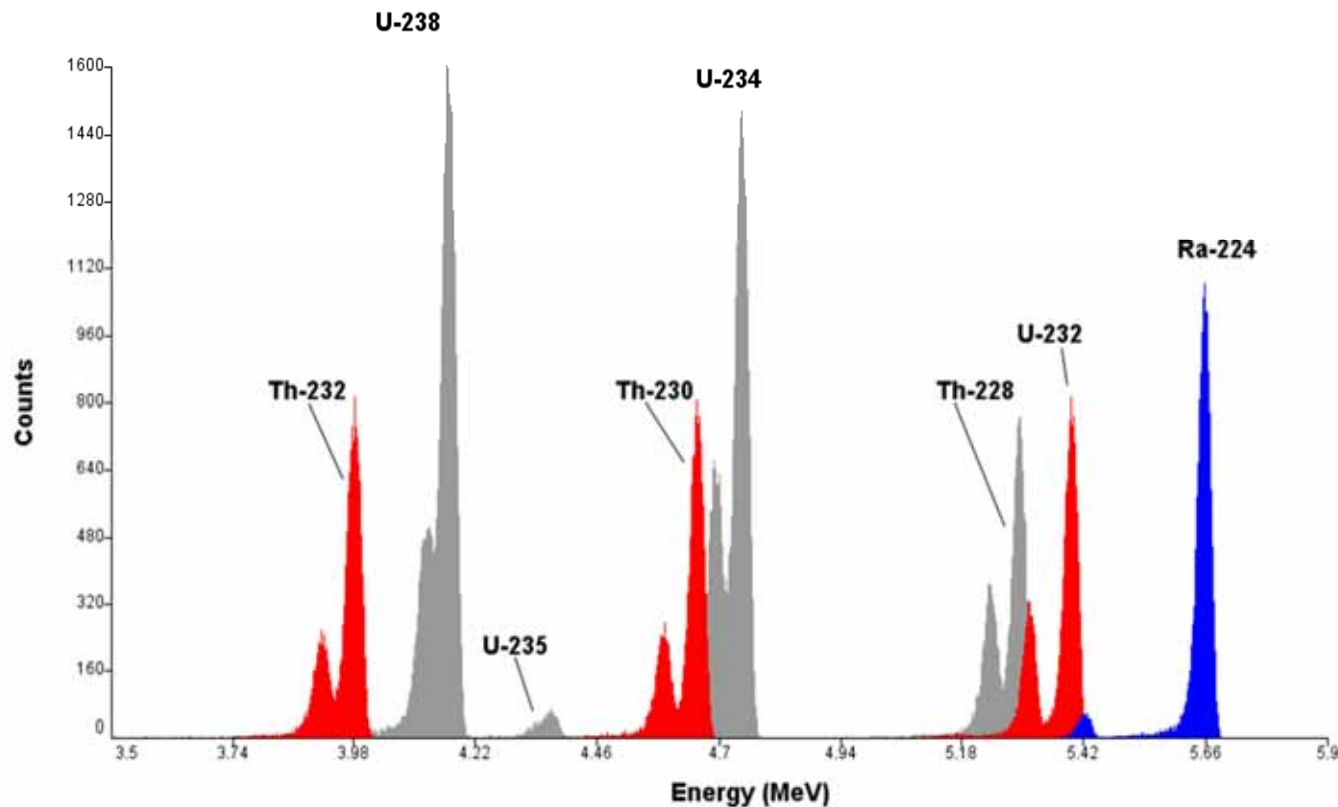
- **Sensitivity (transmission of ions to detector)**
- **Polyatomic interferences & background signals**
- **Abundance sensitivity**
- **Isotope ratios**

Alpha-spectrometry of uranium



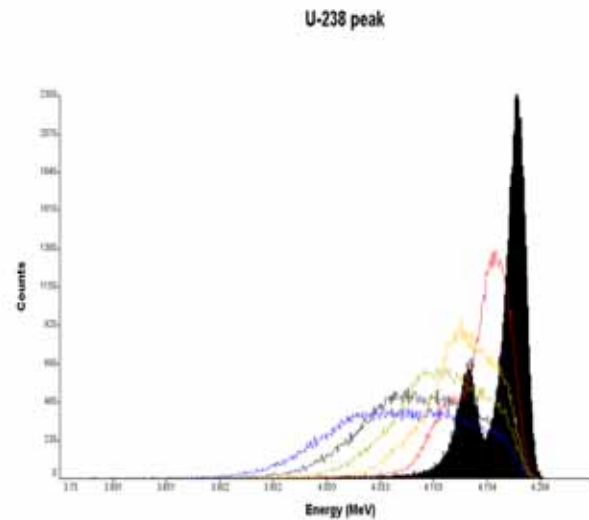
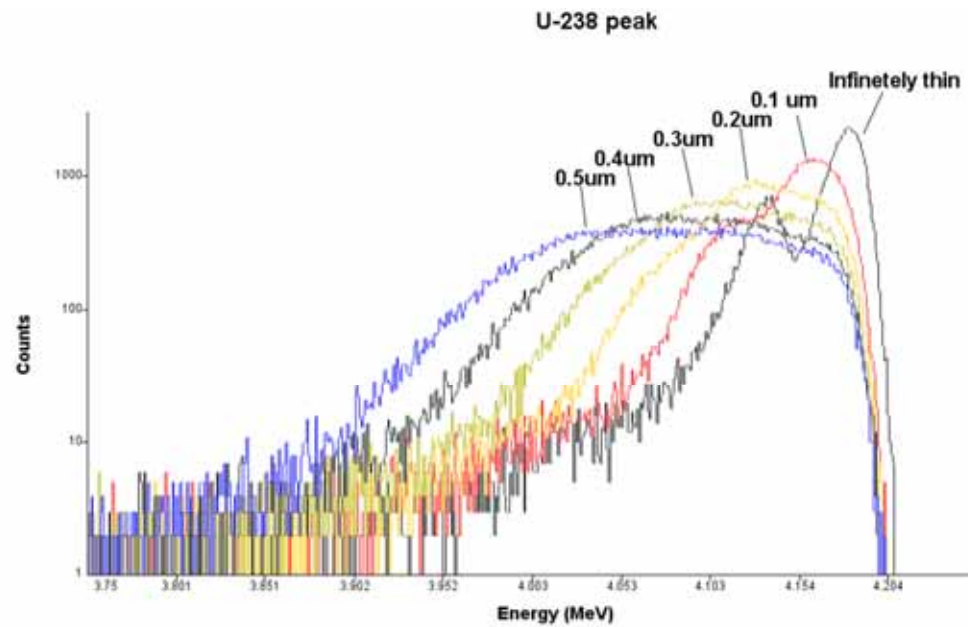
Inteference U&Th isotopes

Chemistry needed to remove matrix and interfering alpha emitters



Alpha-spectra simulated by 'AASI' Monte Carlo

Alpha peak shape and the thickness of electrodeposited material

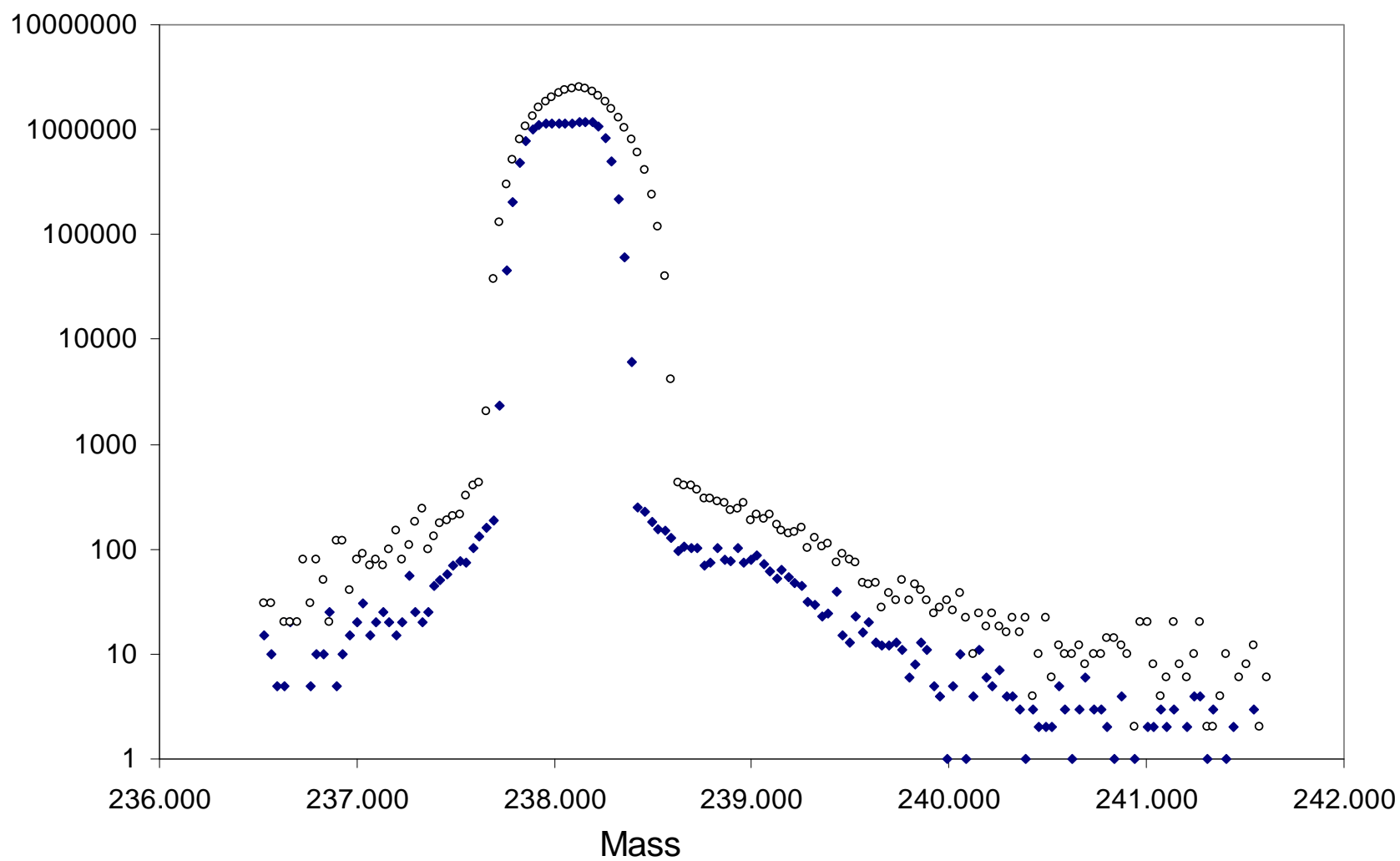


U & Th by mass - extreme ratios

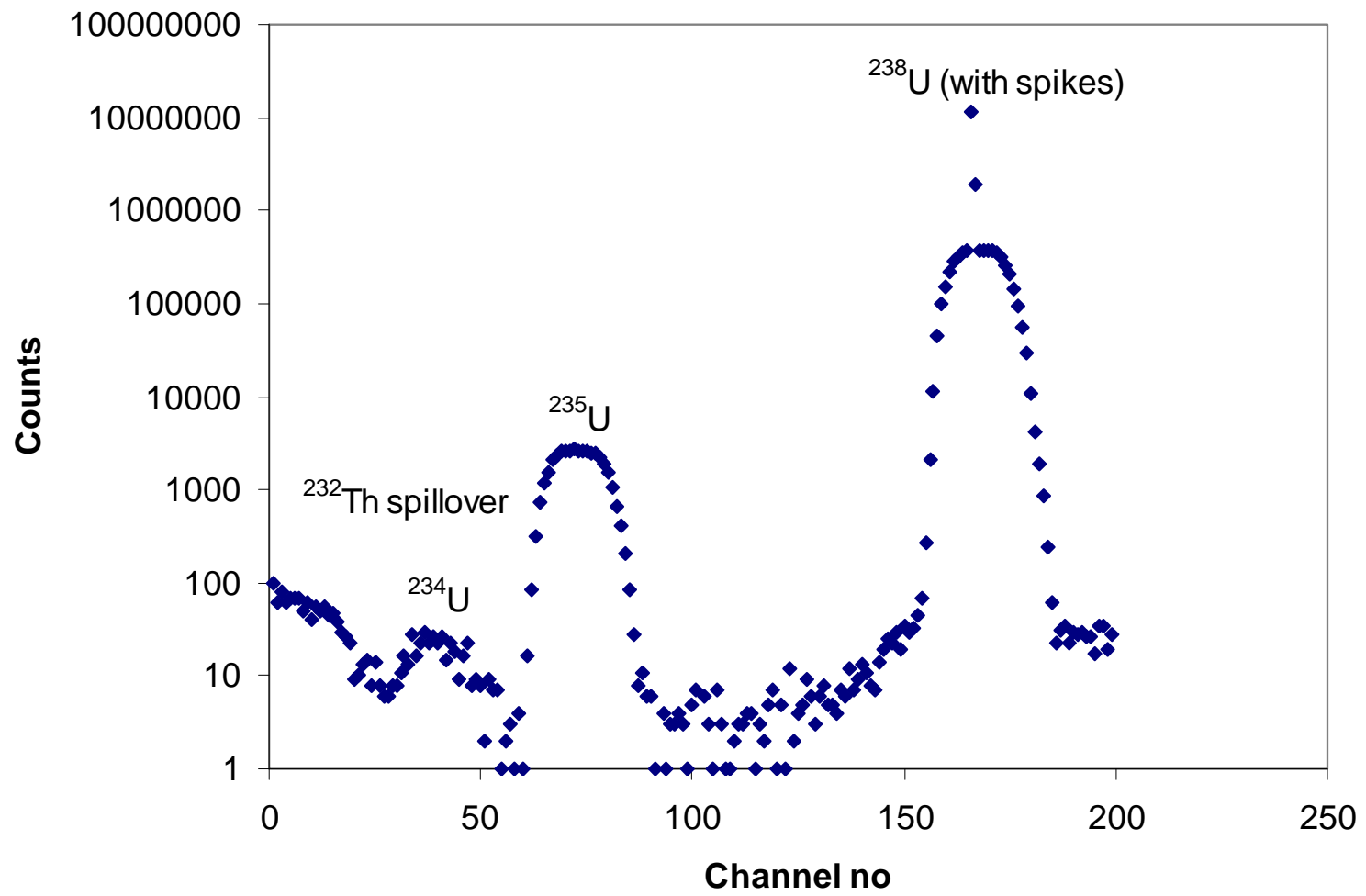
(atom ratios for stable element isotopes at % levels)

	Activity ratio	Atom number ratio
$^{230}\text{Th}/^{232}\text{Th}$	0.2-5	$\sim 10^{-6} - 10^{-5}$
$^{235}\text{U}/^{238}\text{U}$	0.045	0.0072
$^{234}\text{U}/^{238}\text{U}$	0.5-10	$\sim 10^{-5} - 10^{-4}$

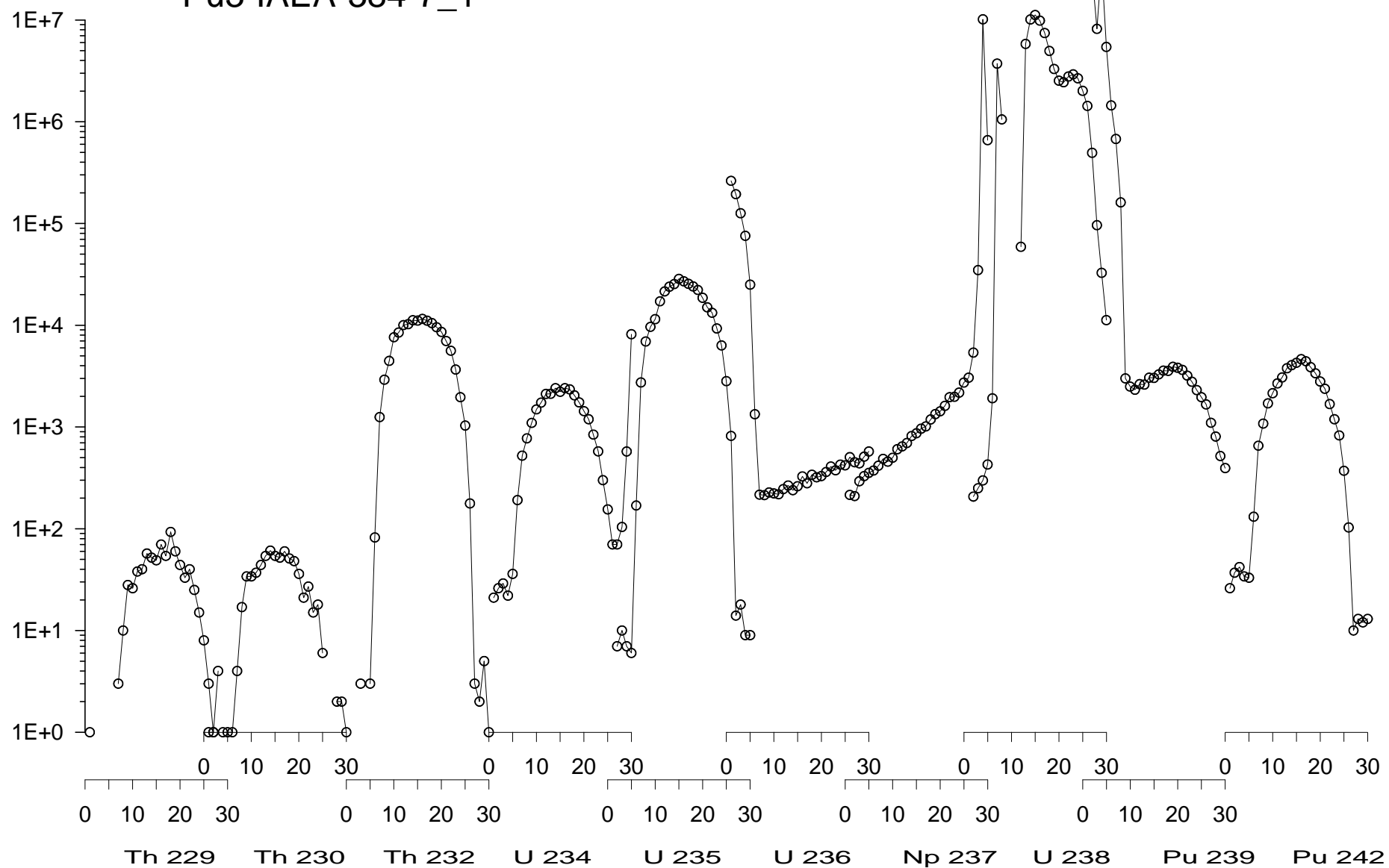
Peak tailing & peak shape



Abundance sensitivity natural uranium in soil. No radiochemistry

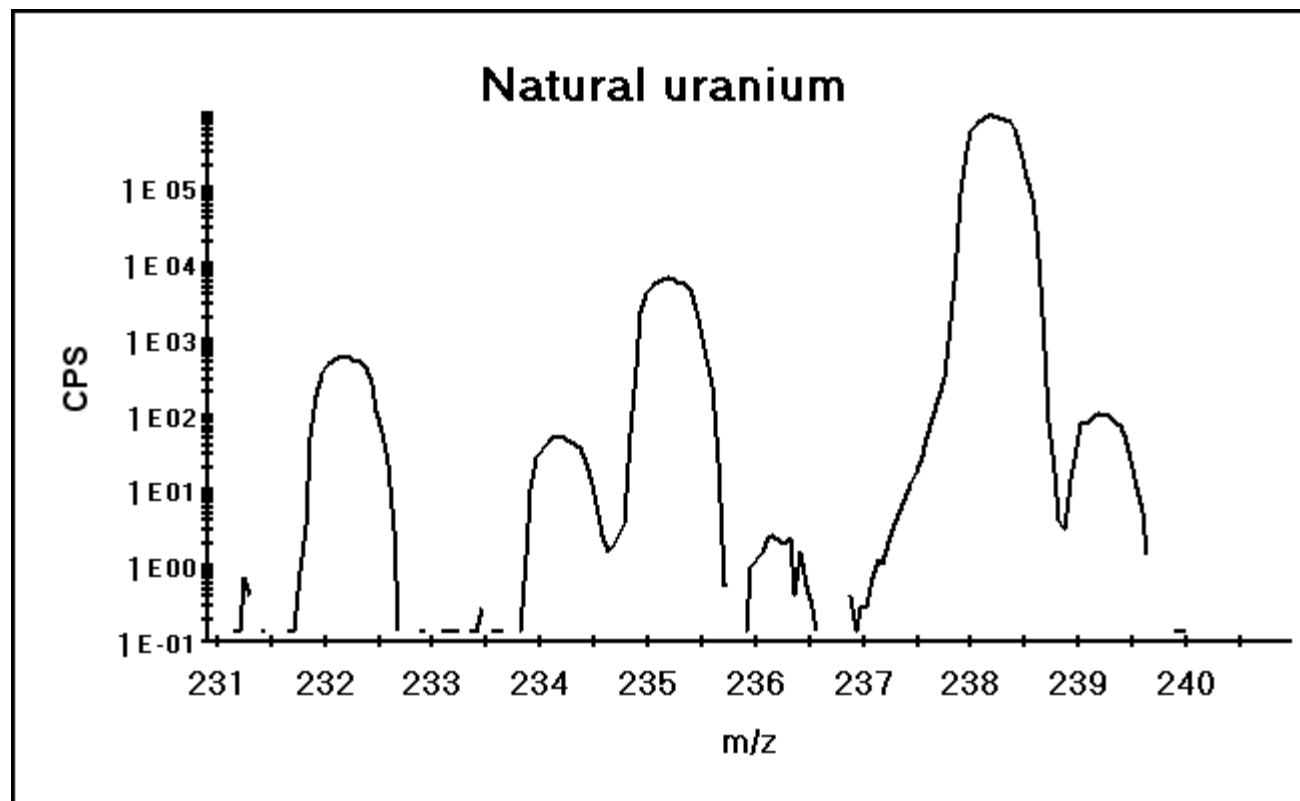


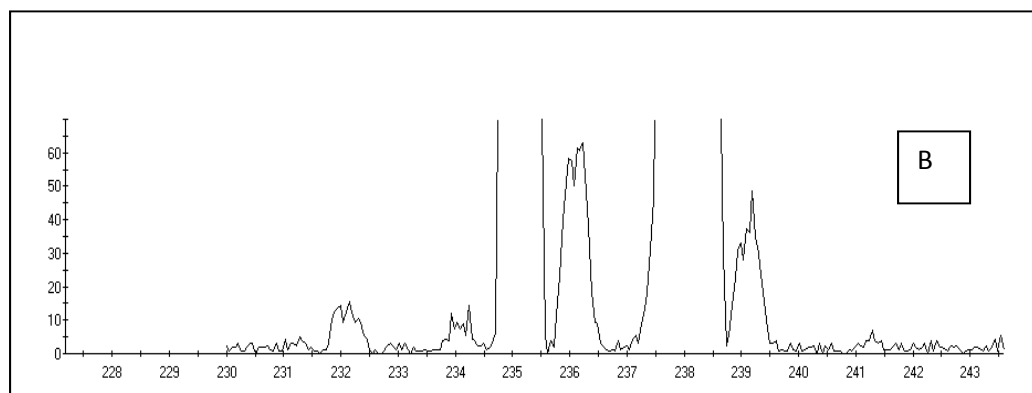
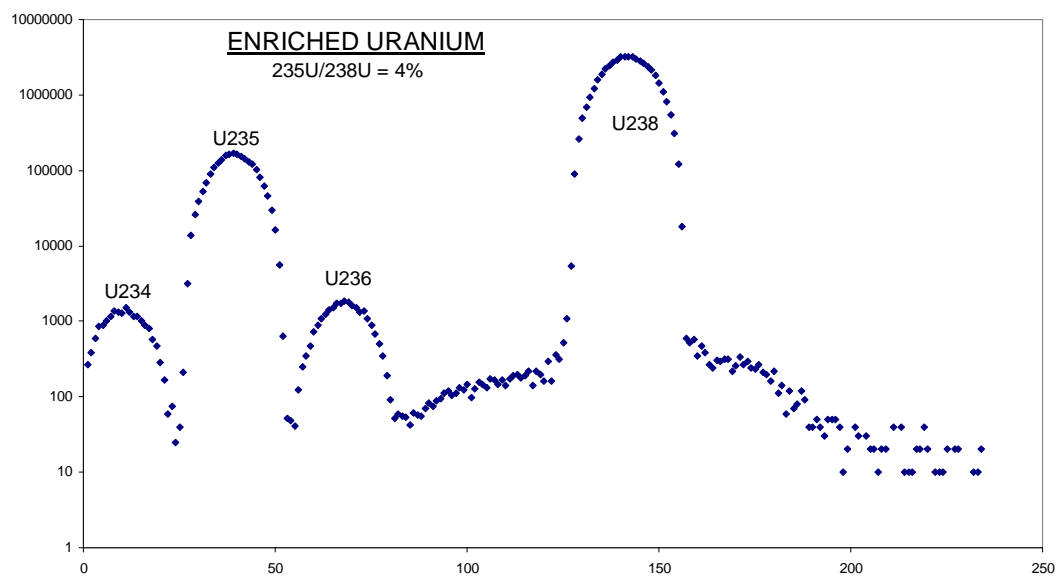
Pu3-IAEA-384-7_1



Peak shape for quadrupole MS

Rounded peak top but very little tailing





Efficiency alpha vs. ICP-MS

- **Alpha**: Geometric efficiency about 25%
- **ICP-MS**: Efficiency about 1: 10 000
- **Alpha counting** of ^{238}U ($4.5 \cdot 10^9\text{y}$). One month counting \Rightarrow about 10^{-12} of the sample atoms have decayed.
- **ICP-MS** measurement of ^{238}U takes about 10 minutes. 10^{-4} of sample atoms are detected.

Different separation chemistry relative to radiometric needs

Table 1
Possible interferences for Pu isotopes and required mass resolution on ICP-SFMS

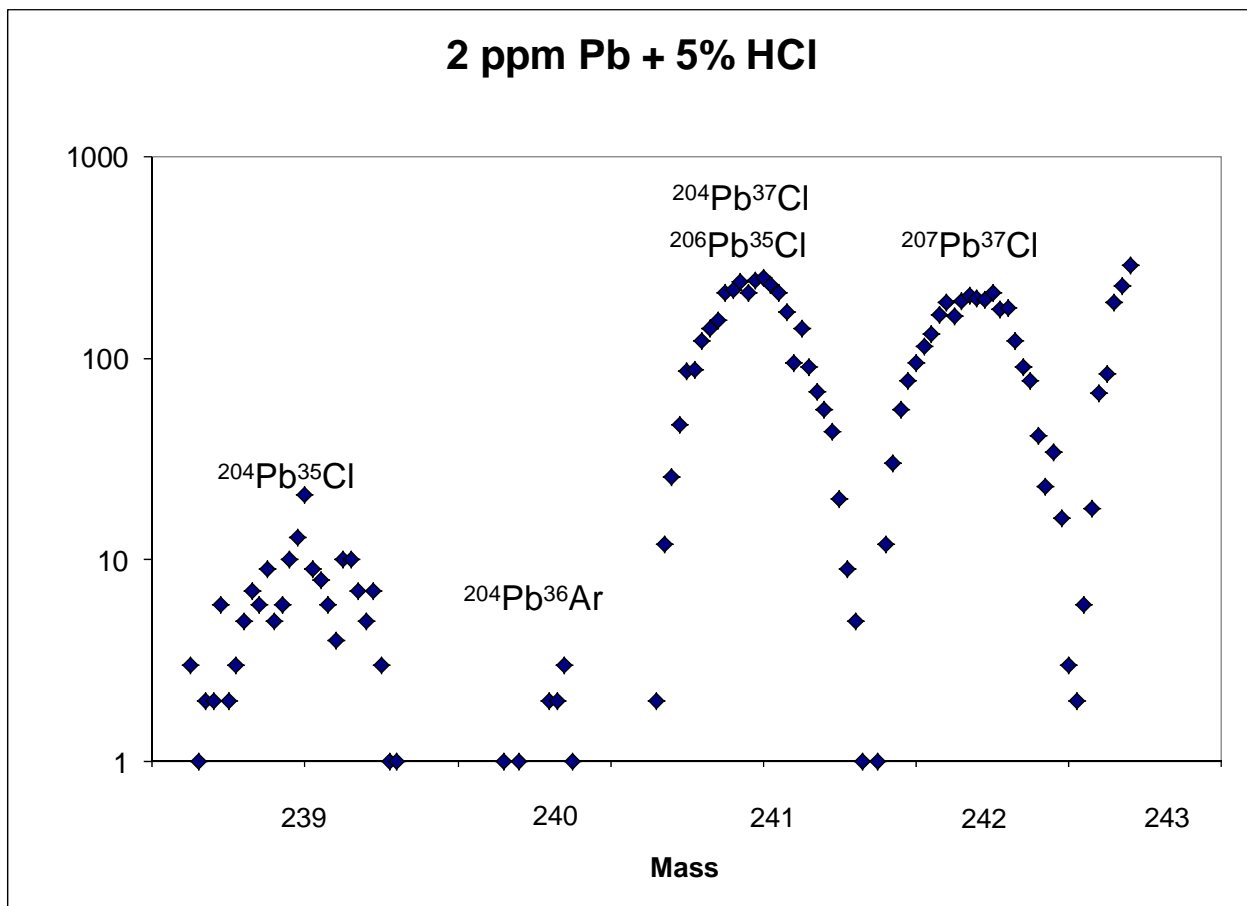
Nuclide	Molecular ions	Required mass resolution, $m/\Delta m$
^{238}Pu	$^{238}\text{U}^+$	193665
	$^{206}\text{Pb}^{16}\text{O}^{14}\text{N}^1\text{H}_2^+$	3874
	$^{208}\text{Pb}^{16}\text{O}^1\text{H}_2^{12}\text{C}^+$	3818
	$^{208}\text{Pb}^{14}\text{N}_2^1\text{H}_2^+$	4654
^{239}Pu	$^{238}\text{U}^1\text{H}^+$	36885
	$^{207}\text{Pb}^{16}\text{O}^{14}\text{N}^1\text{H}_2^+$	3817
	$^{208}\text{Pb}^{16}\text{O}^{14}\text{N}^1\text{H}^+$	3430
^{240}Pu	$^{238}\text{U}^1\text{H}_2^+$	19116
	$^{208}\text{Pb}^{16}\text{O}^{14}\text{N}^1\text{H}_2^+$	3774
^{241}Pu	$^{207}\text{Pb}^{16}\text{O}_2^1\text{H}_2^+$	3193
^{242}Pu	$^{208}\text{Pb}^{16}\text{O}_2^1\text{H}_2^+$	3159
^{244}Pu	$^{206}\text{Pb}^{12}\text{C}_3^1\text{H}_2^+$	3293
	$^{207}\text{Pb}^{12}\text{O}_3^1\text{H}^+$	3031

Table 1
Possible interferences for ^{90}Sr and Pu isotopes and required mass resolution on ICP-SFMS

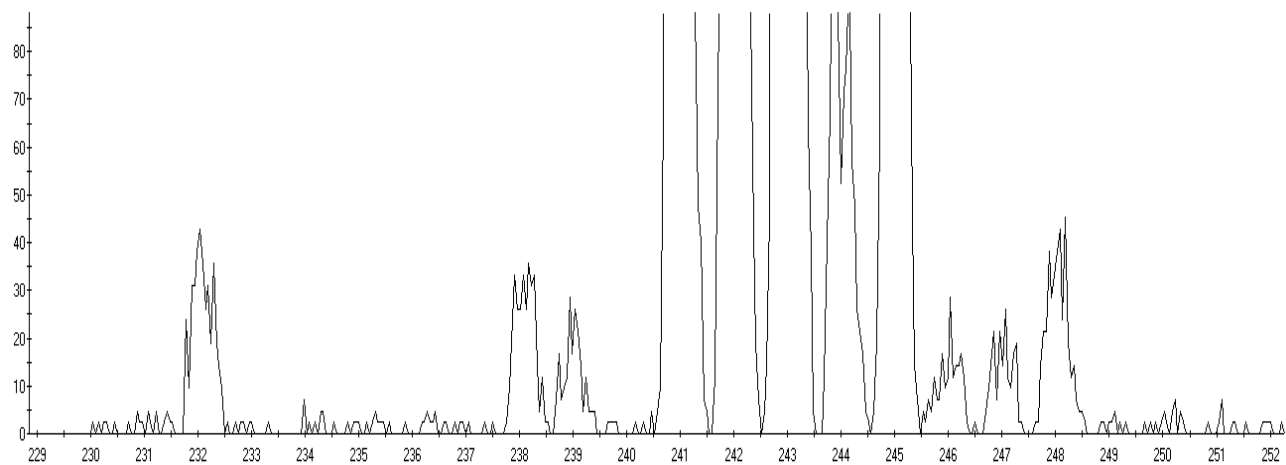
Nuclide	Molecular ions	Required mass resolution ($m/\Delta m$)
^{90}Sr	$^{180}\text{W}^{2+}$	1370
	$^{180}\text{Hf}^{2+}$	1372
	$^{58}\text{Ni}^{16}\text{O}_2^+$	2315
	$^{74}\text{Ge}^{16}\text{O}^+$	10765
	$^{52}\text{Cr}^{38}\text{Ar}^+$	19987
	$^{50}\text{V}^{40}\text{Ar}^+$	49894
	$^{54}\text{Fe}^{36}\text{Ar}^+$	155548
	$^{50}\text{Ti}^{40}\text{Ar}^+$	158287
^{239}Pu	$^{90}\text{Zr}^+$	29877
	$^{238}\text{U}^1\text{H}^+$	36885
	$^{207}\text{Pb}^{16}\text{O}^{14}\text{N}^1\text{H}_2^+$	3817
	$^{208}\text{Pb}^{16}\text{O}^{14}\text{N}^1\text{H}^+$	3430
^{240}Pu	$^{238}\text{U}^1\text{H}_2^+$	19116
	$^{208}\text{Pb}^{16}\text{O}^{14}\text{N}^1\text{H}_2^+$	3774

Plutonium isotopes

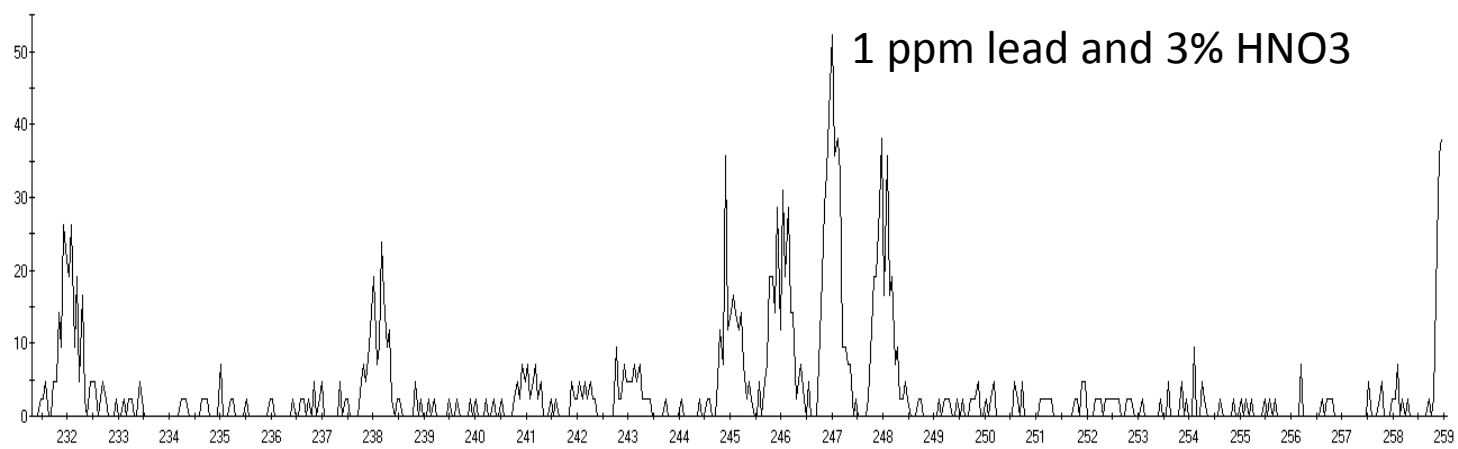
Interferences from clorides



1 ppm lead and 3% HCl



1 ppm lead and 3% HNO₃



Matrix suppression

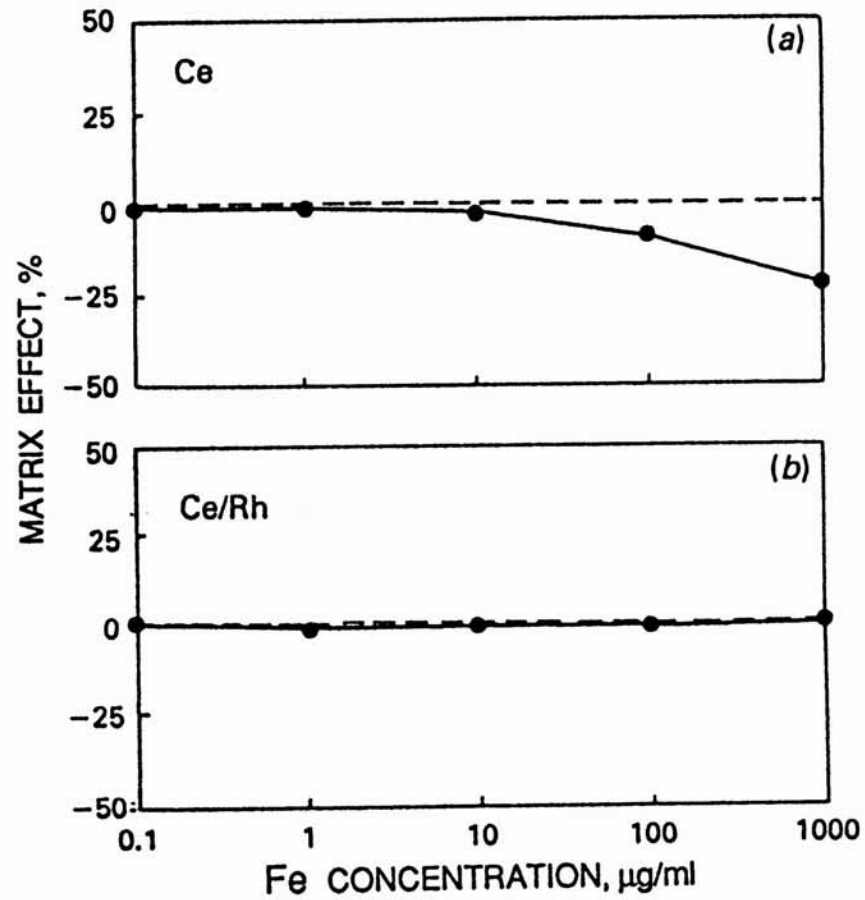
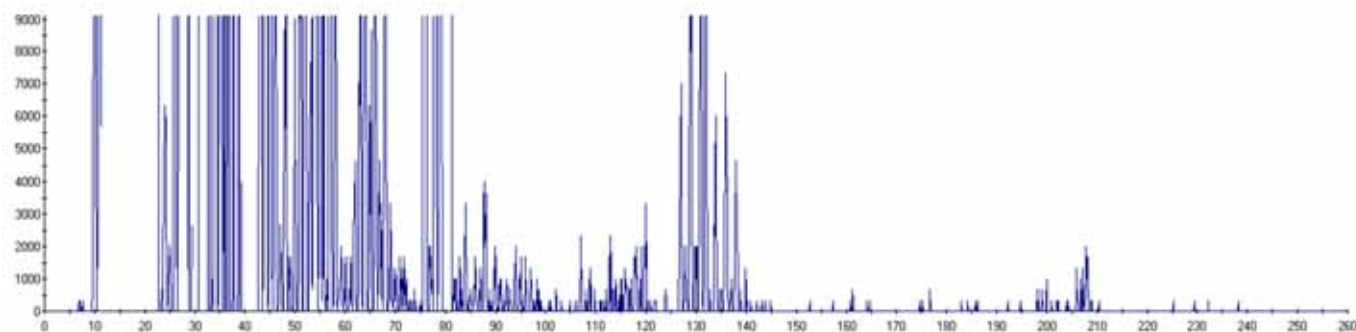
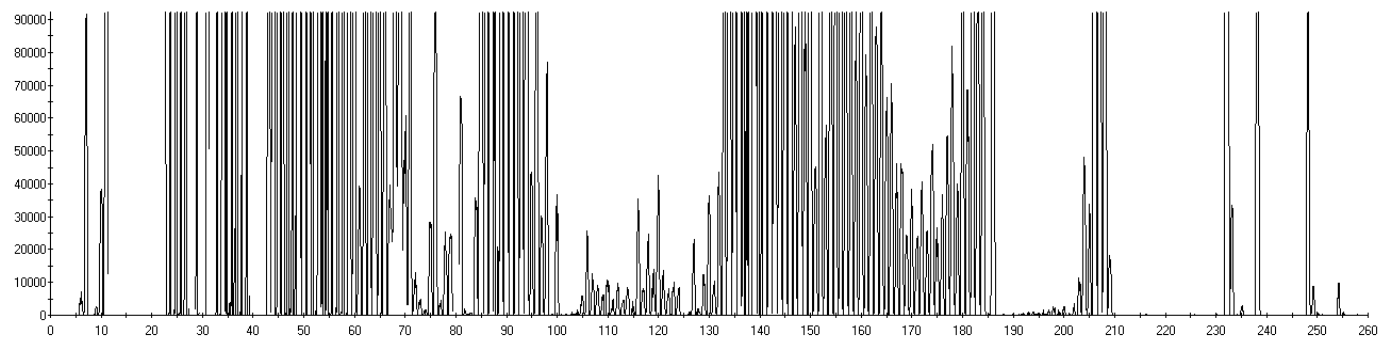


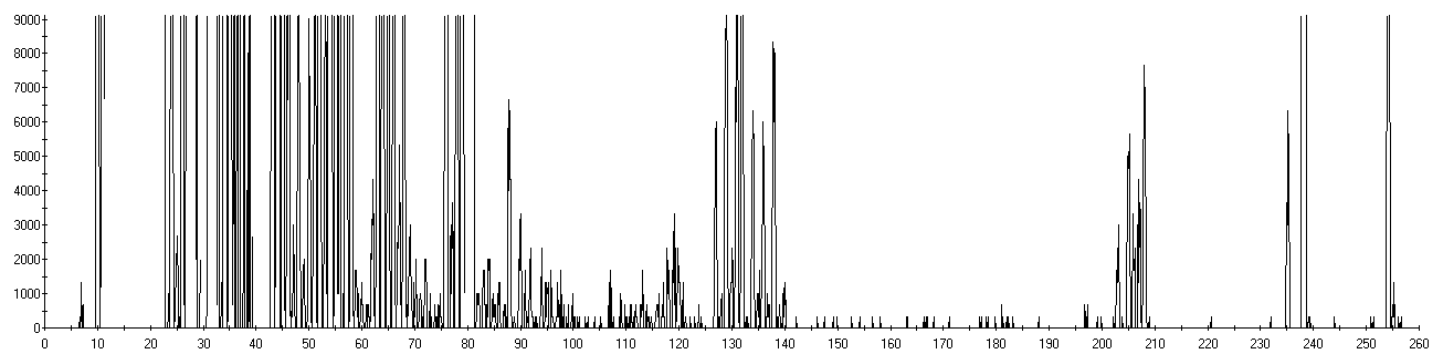
Figure 7.25 Effect of increasing Fe concentration on the Ce signal (a) with and (b) without the use of Rh as internal standard. (From Reference 294, with permission.)



Instrument back-
ground

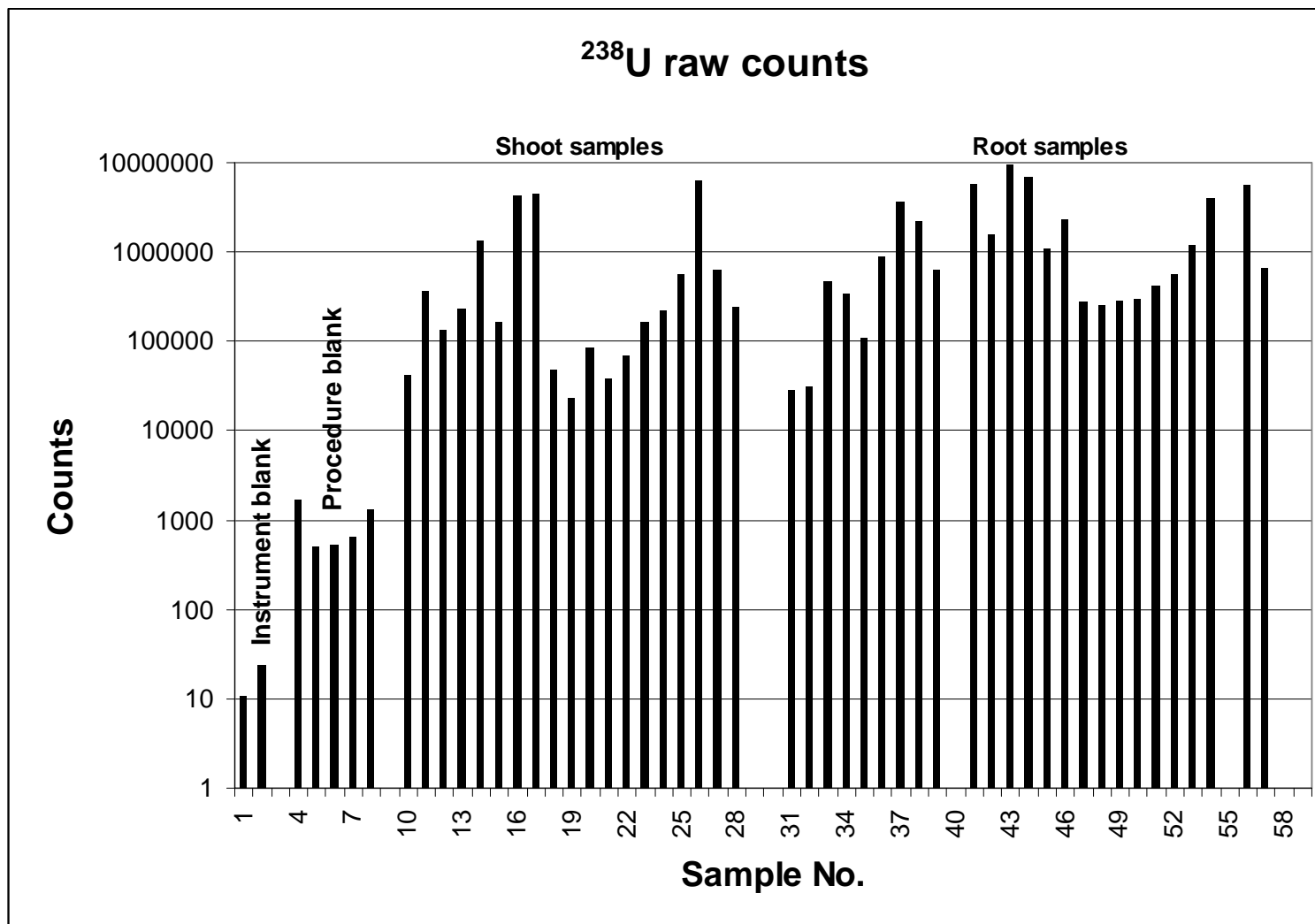


1g sediment
'raw'.



Sample after
TBP-extraction

Negative side in applying chemistry to the sample.....



Problems in isotope ratio measurements (single collectors)

- Sample introduction system
- Plasma instability
- Dead time corrections
- Mass fractionation
- Interferences
- Abundance sensitivity (peak tailing)

